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Chemical composition and antioxidant activity of the coriander cake obtained by extrusion

Jazia Sriti [a,b,*], Iness Bettaieb [a], Olfa Bachrouch [a], Thierry Talou [b], Brahim Marzouk [a]

[a] *Bioactive Substances Laboratory, Biotechnology Center in Borj-Cedria Technopark, BP. 901, 2050 Hammam-Lif, Tunisia*
[b] *Agro-industrial Chemistry Laboratory UMR 1010 INRA/INP, ENSIACET, 4 allee Emile Monso, 31030 Toulouse cedex 4, France*

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Abstract This study was designed to examine the effect of operating conditions on essential oil composition and antioxidant activity of coriander cakes. Twenty-nine components were determined in essential oils, which were mostly alcohol monoterpenes. The highest essential oil yields (0.11%) were obtained by the nozzle diameter of 5 mm. The main components of cake essential oil linalool, γ-terpinene, geranyl acetate, linalyl acetate and camphor showed significant variations with different nozzle diameter.

The total phenol contents and condensed flavonoid contents varied between different nozzle diameters; the highest values obtained of small diameters (5 and 6 mm). Significant differences were also found in total tannin contents among different nozzle diameters. The total phenol contents decreased significantly ($p < 0.05$) when increased the nozzle diameter to 9 mm and reached 9.11 mg GAE/g.

The screening of antioxidant activity of the different coriander cakes using the di(phenyl)-(2,4,6-trinitrophenyl) iminoazanium radical (DPPH) assay showed an appreciable reduction of the stable radical DPPH, although small nozzle diameter was the most efficient method with an IC_{50} reached of 55 μg/ml as compared with bigger diameter (IC_{50} = 88 μg/ml).

All the extracts had lower β-carotene bleaching activity than that of synthetic antioxidant BHA and BHT. Coriander cake extracts presented a very low reducing power ability ($EC_{50} \approx 700$ μg/ml) compared to ascorbic acid (EC_{50} = 40 μg/ml).

* Corresponding author at: Bioactive Substances Laboratory, Biotechnology Center in Borj-Cedria Technopark, BP. 901, 2050 Hammam-Lif, Tunisia. Tel.: +216 79325511; fax: +216 79325855.
E-mail address: sritijazia@yahoo.fr (J. Sriti).

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1. Introduction

Coriander (*Coriandrum sativum* L.), an annual Apiaceae, commonly used as a condiment or a spice in the Mediterranean area. The fruits have been used as a traditional medicine in many cultures to treat various medical conditions,

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including drug for indigestion, against worms and as a component of embrocations for rheumatism and pains in the articulations (Norman, 1990). Coriander fruit has been reported as containing both essential oil (rich in linalool) and vegetal oil (rich in petroselinic acid) (Sriti et al., 2012). In general some work focused on sequenced extractions from coriander fruits respecting the two fractions of interest (vegetal and essential oils), while not penalising the subsequent valorisation of the residual byproduct (Sriti et al., 2009).

In recent years, the exploitation of organic residues has been increased from various sectors of agriculture and industries. The cake oil showed some important applications that have been used for the production of industrial enzymes, antibiotics, biopesticides, vitamins and other biochemical. The importance of the nutritional availability of oil cakes depended on the quality of the seed, method of oil extraction, storage parameters (Ramachandran et al., 2007). The chemical composition of the oil cakes was widely reported in many plants such as: sunflower, sesame, soybean, coconut, mustard, palm kernel, groundnut, cottonseed, canola, olive (Ramachandran et al., 2007). Recent studies on *C. sativum* L. composition analysis have described fatty acid, sterol and tocol composition of the cake obtained after oil extraction from the seeds (Sriti et al., 2012). Darughe et al. (2012) had also determined the essential oil composition, antioxidant and antifungal activity of *C. sativum* in butter cake. However, little researches have undertaken the antioxidant activity of coriander fruit essential oil and extract (Sriti et al., 2011a) and there is no information regarding the cake which obtained by single screw.

The objective of this study was to investigate the effects of nozzle diameters on the chemical composition of *C. sativum* cake. Another goal of the work was to determine the effects of operating conditions on the chemical composition and antioxidant activity of coriander cake.

2. Materials and methods

2.1. Chemicals

All solvents used in these experiments (diethyl ether, chloroform, acetonitrile and methanol) were purchased from Merck (Darmstadt, Germany). Sulphuric acid (H_2SO_4), acetic acid, sodium hydroxide (NaOH), hydrochloric acid (HCl), sodium carbonate (Na_2CO_3), sodium nitrite ($NaNO_2$), butylated hydroxytoluene (BHT), 1,1-diphenyl-2-picrylhydrazyl (DPPH), polyvinyl polypyrrolidone Folin-Ciocalteu reagent and aluminium chloride ($AlCl_3$) were purchased from Sigma–Aldrich (Steinheim, Germany).

2.2. Plant material

All trials were carried out using a single batch of coriander fruits obtained from Korba area (Northwestern Tunisia; latitude 36°34″38.22″(N); longitude 10°51″29.63″(E); altitude 637 m). In this study, the fruits from coriander were extracted with single screw press extruder, the cake samples were immediately collected for further analysis.

2.3. Extrusion

Extrusion was done by a Single-screw (Model OMEGA 20, France) with a motor (0.75 kW, 230 V of maximal tension, 5.1 A of maximal intensity), a screw length of 18 cm, a pitch screw of 1.8 cm, with an internal diameter of 1.4 cm, a channel depth of 0.5 cm and a sleeve of 2.5 cm of internal diameter equipped with a filter-pierced outlet for liquid at the end of the screw and at the surface of the nozzles. The filter section was of 2 mm in diameter to separate extracted oil. The feed rate and the screw rotation speed were maintained constant to 15 g/min (0.9 kg/h) and 40 rpm, respectively. Five nozzles of different diameters (5, 6, 7, 8 and 9 mm) were used in the pressing of the coriander seed. The nozzle/screw distance was 3 cm. The screw press was first run for 15 min without seed material but with heating via an electrical resistance-heating ring attached around the press barrel, to raise the screw press barrel temperature to the desired value. Running temperature was adjusted with a thermocouple (Sriti et al., 2011b).

2.4. Essential oil extraction

The cake (300 g of dry matter) recuperated under extrusion was hydrodistilled for 6 h using a Clevenger apparatus and the yield of volatile oil was calculated for meal sample. The obtained essential oil was dried over anhydrous sodium sulphate, then stored at 4 °C until it is tested and analysed.

2.5. Gas chromatography–flame ionisation detector (GC–FID) analysis

Essential oils were analysed by gas chromatography (GC) using a Hewlett–Packard 6890 apparatus (Agilent Technologies, Palo Alto, CA, USA) equipped with a flame ionisation detector (FID) and an electronic pressure control (EPC) injector. A HP-Innowax capillary column (polyethylene glycol: 30 m × 0.25 mm i.d ×0.25 mm film thickness; Agilent Technologies, Hewlett–Packard, CA, USA) was used; the flow of the carrier gas (N_2, U) was 1.6 ml/min. Analyses were performed using the following temperature programme: oven isotherm at 35 °C during 10 min, from 35 to 205 °C at the rate of 3 °C/min and isotherm at 205 °C during 10 min. Injector and detector temperatures were held, respectively, at 250 and 300 °C. Diluted samples of 2.0 µl were injected in the split/splitless mode (60:1 split) mode.

2.6. Gas chromatography–mass spectrometry (GC–MS)

The GC–MS analyses were performed on a gas chromatograph HP 5890 (II) interfaced with an HP 5973 mass spectrometer (Agilent Technologies, Palo Alto, California, USA) with electron impact ionisation (70 eV). A HP-5MS capillary column (60 m × 0.25 mm, 0.25 µm film thickness) was used. The column temperature was programmed to rise from 40 to 280 °C at a rate of 5 °C/min. The carrier gas was Helium with a flow rate of 1.2 ml/min. Scan time and mass range were 1 s and 50–550 m/z., respectively. The injected volume was 1 µl and the total run time was approximately 63 min.

Identification of the oil constituents was based on the comparison of their retention indexes relative to C8–C22 n-alkanes

with those in the literature or with those of authentic compounds available in our laboratory. Further identification was made by matching their recorded spectra with those stored in the Wiley/NBS mass spectral library of the GC–MS data system and other published mass spectra (Adams, 2001).

2.7. Preparation of extracts

The air-dried coriander cake was finely grounded with a blade-carbide gringing (IKA-WERK Type: A: 10). Triplicate subsamples of 2.5 g of each ground sample were separately extracted by stirring with 10 ml of pure methanol for 30 min. The extracts were then kept for 24 h at 4 °C, filtered through a Whatman No. 4 filter paper, evaporated under vacuum to dryness and stored at 4 °C until their analysis (Mau et al., 2001).

2.8. Total phenolic content

Total phenolic contents were assayed using the Folin–Ciocalteu reagent, following Singleton's method slightly modified by Dewanto et al. (2002). An aliquot (0.125 ml) of a suitable diluted methanolic cake extract was added to 0.5 ml of deionised water and 0.125 ml of the Folin–Ciocalteu reagent. The mixture was shaken and allowed to stand for 6 min, before adding 1.25 ml of 7% Na_2CO_3 solution.

The solution was then adjusted with deionised water to a final volume of 3 ml and mixed thoroughly. After incubation for 90 min at 23 °C, the absorbance versus prepared blank was read at 760 nm. Total phenolic contents of coriander cakes (three replicates per treatment) were expressed as mg gallic acid equivalents per gram (mg GAE/g) through the calibration curve with gallic acid. The calibration curve range was 50–400 mg/ml ($R^2 = 0.99$). All samples were performed in triplicates.

2.9. Total flavonoid content

Total flavonoid contents were measured according to the method of Dewanto et al. (2002). A total of 250 μl of methanolic extract was mixed with 75 μl $NaNO_2$ (5%). After 6 min, 150 μl of 10% $AlCl_3$ and 500 μl of NaOH (1 M) were added to the mixture. Finally, the mixture was adjusted to 2.5 ml with distilled water. The absorbance versus prepared blank was read at 510 nm. Total flavonoid contents of cakes (three replicates per treatment) were expressed as mg catechin equivalents per gram (mg CE/g) through the calibration curve with catechin. The calibration curve range was 50–500 mg/ml. Triplicate measurements were taken for all samples.

2.10. Condensed tannin content

The total tannin content was measured using the modified vanillin assay described by Sun et al. (1998). A total of 3 ml of 4% methanol vanillin solution and 1.5 ml of concentrated H_2SO_4 were added to 50 μl of suitably diluted sample. The mixture was kept for 15 min, and the absorbance was measured at 500 nm against methanol as a blank. The amount of total condensed tannins was expressed as milligrams of (+)-catechin equivalent per gram of dry weight (mg of CE/g of DW) through the calibration curve with catechin. Triplicate measurements were taken for all samples.

2.11. DPPH assay

The donation capacity of the obtained extracts was measured by bleaching of the purple-coloured solution of the DPPH radical according to the method of Hanato et al. (1998). A total of 1 mL of different concentrations of extracts prepared in 80% acetone was added to 0.5 ml of a 0.2 mmol/l DPPH methanolic solution. The mixture was shaken vigorously and kept at room temperature for 30 min. The absorbance of the resulting solution was then measured at 517 nm after 30 min. The antiradical activity was expressed as IC_{50} (μg/ml), the concentration required to cause 50% DPPH inhibition. The ability to scavenge the DPPH radical was calculated using the following equation:

$$\text{DPPH scavenging effect}(\%) = [(A_0 - A_1)/A_0] \times 100$$

where A_0 is the absorbance of the control at 30 min, and A_1 is the absorbance of the sample at 30 min. BHT was used as a positive control. Tests were carried out in triplicate.

2.12. β-Carotene bleaching test

A modified method described by Koleva et al. (2002) was employed. β-Carotene (2 mg) was dissolved in 20 ml of chloroform. Then, 4 ml of this solution was added to linoleic acid (40 mg) and Tween 40 (400 mg). Chloroform was evaporated under vacuum at 40 °C, and 100 ml of oxygenated ultrapure water was added. Then, the emulsion was vigorously shaken. Reference compounds [BHT and butylated hydroxyanisole (BHA)] and sample extracts were prepared in methanol. The emulsion (3 ml) was added to a tube containing 0.2 ml of different concentrations of essential oils and extract. The absorbance was immediately measured at 470 nm, and the test emulsion was incubated in a water bath at 50 °C for 120 min, when the absorbance was measured again. BHT and BHA were used as a positive control. In the negative control, the essential oil or the extract was substituted with an equal volume of methanol. The antioxidant activity (%) of the acetone extracts and essential oils was evaluated in terms of the bleaching of the β-carotene using the following formula:

$$\text{percent inhibition}(\%) = [(A_t - C_t)/(C_0 - C_t)] \times 100$$

where A_t and C_t are the absorbance values measured for the test sample and control, respectively, after incubation for 120 min, and C_0 is the absorbance values for the control measured at zero time during the incubation. The results are expressed as IC_{50} values (μg/ml), the concentration required to cause a 50% β-carotene bleaching inhibition. Tests were carried out in triplicate.

2.13. Reducing power

The method of Oyaizu (1986) was used to assess the reducing power of different cake extracts. A total of 1 ml of different concentrations of extracts in 80% acetone was mixed with 2.5 ml of a 0.2 M sodium phosphate buffer (pH 6.6) and 2.5 ml of 1% potassium ferricyanide [$K_3Fe(CN)_6$] and incubated in a water bath at 50 °C for 20 min. Then, 2.5 ml of 10% trichloroacetic acid was added to the mixture that was centrifuged at 650*g* for 10 min. The supernatant (2.5 ml) was then mixed with 2.5 ml of distilled water and 0.5 ml of 0.1%

ferric chloride solution. The intensity of the blue–green colour was measured at 700 nm. The EC_{50} value (mg/ml) is the extract concentration at which the absorbance was 0.5 for the reducing power and was calculated from the graph of absorbance at 700 nm against extract concentration. Ascorbic acid was used as a positive control. Tests were carried out in triplicate.

2.14. Statistical analysis

All extractions and determinations were conducted in triplicate. Data are expressed as mean (standard deviation (SD). The means were compared by using the one way followed by Duncan's multiple range tests. Individual means were deemed to be significant at $p \leqslant 0.05$. A Cluster Analysis (CA) was performed in order to discriminate between different nozzle diameters on the basis of their essential oil composition. All analyses were performed by the 'Statistica v 5.1' software (Stasoft, 1998).

3. Results and discussion

3.1. Effect of operating conditions on essential oil yield

The variation of coriander cake essential oil yield as affected by nozzle diameter is illustrated in Fig. 1. Results showed that the essential oil yield of cake decreases significantly by about 0.11% and 0.04% for 5 mm and 9 mm of nozzle diameter, respectively. It can be explained that the elevation of nozzle diameter contributes to the decrease of pressure on the matter. On the other hand, the decrease in the essential oil yield can be attributed to the fact that the temperature increased similarly to the extracting pressure.

According to Buggle et al. (1999), increasing temperature resulted in decreasing in essential oil content of Cymbopogon citratus (DC) Stapf. Similar results have been also reported by Braga et al. (2005) in *Piper hispidinervium* C.DC and by Khangholi and Rezaeinodehi (2008) in *Artemisia annua* plants as affected by drying method.

The essential oil yield in coriander fruit before extrusion was 0.37%. Vegetable oil extraction processes therefore reduce the essential oil yield, which is not surprising given the volatile nature of most components of essential oils.

3.2. Chemical composition of coriander cake

Effects of extrusion conditions on the essential oil composition of coriander cake are shown in Table 1.

The GC and GC–MS analysis of these oils resulted in the identification of 39 constituents, representing 70–95% of the oils.

Significant changes ($p < 0.05$) were observed in the chemical profile of the essential oils. Nevertheless, monoterpene alcohols remained the major class (54–79%) followed by monoterpene esters (4–10%), hydrocarbons (1–14%), monoterpene Ketones (1–3%), monoterpene aldehydes (0.31–0.52%), sesquiterpenes (0.25–0.81%), monoterpene ethers (0.14–0.30%) and phenols (0.05–0.34%). In contrast, the relative percentages of the individual volatiles varied significantly ($p < 0.05$) under different nozzle sizes. Linalool was the major compound of essential oils from all the trials and it reached a maximum at the nozzle diameter of 6 mm (76.11%).

The second main compound, geranyl acetate, increased as the nozzle diameter increased where the highest percentage was registered at 9 mm with 7.45% and its lowest percentage was detected in the trial of 7 mm of nozzle diameter (3.43%). The γ-terpinene reached a maximum percentage at nozzle diameter of 7 mm with 7.63%. As for linalyl acetate, it decreased significantly in the bigger nozzle diameter (9 mm) and its highest percentage was obtained in the trial of small nozzle (5 mm) where it reached 4.04% of total volatiles. The rates of camphor decreased in the trial of nozzle diameter at 6 mm and 9 mm whereas, the percentages of α-pinene increased significantly in the trial of nozzle diameter at 8 mm (4.63%) and decreased using the small diameter (5 and 6 mm).

The variation of individual compounds under the effect of nozzle diameter affects the composition of the different chemical classes. The percentages of monoterpene alcohols and hydrocarbons decreased significantly ($p < 0.05$) and reached its lowest value (54.57% and 1.87%, respectively) in the trial of 9 mm in diameter. However, the rates of monoterpene ester increased under nozzle diameter of 9 mm (10.15%) whereas they decreased under the other nozzle diameter. The highest level of sesquiterpenes was detected in the diameter of nozzle 9 mm. As for monoterpene ketones, this class decreased only under nozzle diameter 9 mm (1.92%). Finally, phenols

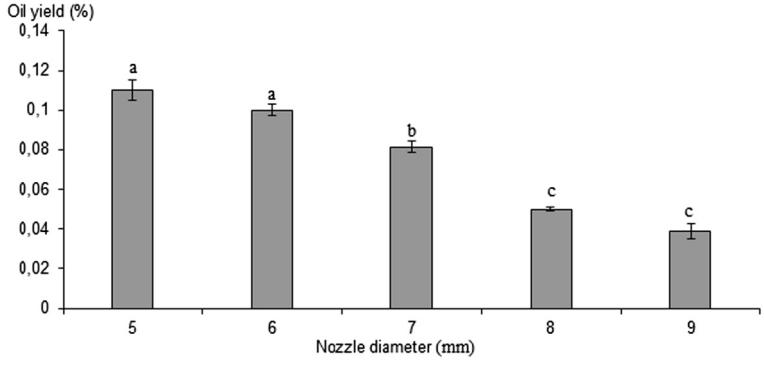

Figure 1 Effects of nozzle diameter on the essential oil yield (%) of *Coriandrum sativum* cake. Oil yield values with different subscript (a–c) were significantly different at $p < 0.05$ (Duncan test).

Table 1 Effect of nozzle diameter on essential oil composition (%) of coriander cake.

Compound[c]	RI[a]	RI[b]	Nozzle diameter (mm)					Identification
			5	6	7	8	9	
Tricyclene	924	1014	0.06 ± 0.02a	0.07 ± 0.01a	tr	–	–	GC–MS
Heptanal	901	1194	0.05 ± 0.01b	tr	0.26 ± 0.02a	0.06 ± 0.01b	–	GC–MS
α-Thujene	931	1035	0.07 ± 0.01a	tr	0.31 ± 0.01b	0.10 ± 0.01c	–	GC–MS
α-Pinene	939	1032	0.31 ± 0.01c	0.14 ± 0.02d	2.81 ± 0.12b	4.63 ± 0.10a	tr	GC–MS, Co-GC
Camphene	954	1076	tr	tr	0.21 ± 0.02a	tr	–	GC–MS
Sabinene	976	1132	0.13 ± 0.02a	0.05 ± 0.02c	0.07 ± 0.03b	tr	tr	GC–MS
β-Pinene	980	1118	0.19 ± 0.01a	0.12 ± 0.01b	tr	0.11 ± 0.01b	tr	GC–MS, Co-GC
Myrcene	991	1174	0.21 ± 0.02b	0.11 ± 0.02c	0.59 ± 0.02a	0.55 ± 0.04a	0.16 ± 0.01b	GC–MS
Decanal	1000	1498	0.05 ± 0.00a	tr	tr	tr	tr	GC–MS
δ-3-Carene	1011	1159	tr	–	–	–	tr	GC–MS
α-Terpinene	1018	1188	0.06 ± 0.02b	0.61 ± 0.03a	0.08 ± 0.02b	0.09 ± 0.02b	–	GC–MS
Limonene	1030	1203	1.04 ± 0.02a	0.02 ± 0.01d	1.19 ± 0.11a	0.52 ± 0.01b	0.14 ± 0.02c	GC–MS, Co-GC
p-Cymene	1026	1280	0.44 ± 0.04b	0.29 ± 0.02c	1.31 ± 0.07a	0.52 ± 0.02b	0.21 ± 0.02c	GC–MS, Co-GC
1,8-Cineole	1033	1213	–	0.12 ± 0.01b	0.23 ± 0.01a	0.11 ± 0.01b	0.06 ± 0.02c	GC–MS, Co-GC
γ-Terpinene	1062	1266	4.13 ± 0.11b	1.98 ± 0.11c	7.63 ± 0.22a	3.46 ± 0.05b	1.13 ± 0.23c	GC–MS, Co-GC
cis-Linalool oxide	1074	1478	tr	tr	tr	tr	0.08 ± 0.02a	GC–MS
trans-Linalool oxide	1088	1450	0.13 ± 0.03a	0.08 ± 0.0a	tr	tr	tr	GC–MS
Linalool	1098	1553	69.06 ± 0.75b	76.11 ± 0.93a	69.94 ± 0.84b	55.14 ± 1.43c	52.05 ± 1.23c	GC–MS, Co-GC
Camphor	1143	1532	3.10 ± 0.08a	1.98 ± 0.23b	2.17 ± 0.05b	2.33 ± 0.02b	1.26 ± 0.02c	GC–MS
Borneol	1165	1719	1.24 ± 0.06a	0.74 ± 0.03b	0.54 ± 0.02c	0.71 ± 0.03b	0.65 ± 0.03b	GC–MS
Terpinen-4-ol	1178	1611	0.69 ± 0.02a	0.27 ± 0.01b	0.21 ± 0.00b	0.37 ± 0.02b	0.06 ± 0.00c	GC–MS, Co-GC
p-Cymen-8-ol	1183	1864	0.59 ± 0.07a	0.18 ± 0.03c	0.18 ± 0.01c	0.39 ± 0.01b	0.32 ± 0.00b	GC–MS, Co-GC
α-Terpineol	1189	1706	2.26 ± 0.32a	1.66 ± 0.05b	0.33 ± 0.02e	0.47 ± 0.02d	0.82 ± 0.02c	GC–MS, Co-GC
Nerol	1228	1797	0.11 ± 0.03a	0.05 ± 0.01b	tr	tr	tr	GC–MS
β-Citronellol	1228	1772	0.33 ± 0.11a	0.20 ± 0.02b	0.12 ± 0.00c	0.07 ± 0.02c	0.25 ± 0.01a	GC–MS, Co-GC
Neral	1240	1694	0.18 ± 0.04a	0.10 ± 0.00b	0.07 ± 0.02b	0.18 ± 0.02a	0.14 ± 0.03a	GC–MS
Carvone	1242	1751	0.86 ± 0.12a	0.77 ± 0.05a	tr	0.35 ± 0.02c	0.66 ± 0.03b	GC–MS, Co-GC
Geraniol	1255	1857	0.09 ± 0.02e	0.22 ± 0.02b	0.24 ± 0.04b	0.17 ± 0.00c	0.37 ± 0.02a	GC–MS, Co-GC
Linalyl acetate	1257	1556	4.04 ± 0.55a	2.43 ± 0.13b	1.35 ± 0.08c	1.01 ± 0.04c	2.70 ± 0.12b	GC–MS
Geranial	1270	1742	0.37 ± 0.03a	0.46 ± 0.02a	0.09 ± 0.01c	0.22 ± 0.01b	0.49 ± 0.02a	GC–MS
Anethole	1283	1228	0.10 ± 0.00c	0.51 ± 0.04a	0.10 ± 0.00c	0.08 ± 0.01c	0.36 ± 0.03b	GC–MS
Thymol	1290	2198	0.29 ± 0.02a	0.25 ± 0.01a	tr	tr	tr	GC–MS, Co-GC
Carvacrol	1292	2239	0.05 ± 0.01a	0.01 ± 0.00a	tr	tr	tr	GC–MS
Eugenol	1356	2192	0.15 ± 0.01a	tr	tr	0.05 ± 0.01b	0.06 ± 0.01b	GC–MS, Co-GC
Geranyl acetate	1383	1765	5.61 ± 0.21b	3.80 ± 0.06c	3.43 ± 0.18c	5.85 ± 0.15b	7.45 ± 0.33a	GC–MS, Co-GC
β-Caryophyllene	1418	1612	0.16 ± 0.00c	0.29 ± 0.02b	0.10 ± 0.00c	0.26 ± 0.03b	0.45 ± 0.04aa	GC–MS
α-Humulene	1454	1687	0.09 ± 0.01c	0.39 ± 0.03b	0.55 ± 0.02a	tr	0.36 ± 0.05b	GC–MS, Co-GC
Monoterpene hydrocarbons			6.67 ± 0.06c	3.44 ± 0.22d	14.26 ± 0.31a	10.07 ± 0.11b	1.87 ± 0.06e	
Monoterpene alcohols			74.41 ± 0.45a	79.45 ± 0.72a	71.61 ± 0.34a	57.35 ± 0.48b	54.57 ± 0.32b	
Monoterpene esters			9.64 ± 0.65a	6.23 ± 0.08b	4.79 ± 0.22c	6.86 ± 0.09b	10.15 ± 0.87a	
Monoterpene aldehydes			0.48 ± 0.06a	0.50 ± 0.10a	0.35 ± 0.01b	0.31 ± 0.00b	0.52 ± 0.02a	
Monoterpene Ketones			3.98 ± 0.05a	2.75 ± 0.04b	2.21 ± 0.06b	2.69 ± 0.01b	1.92 ± 0.02b	
Sesquiterpenes			0.25 ± 0.02c	0.68 ± 0.10b	0.65 ± 0.02b	0.30 ± 0.01c	0.81 ± 0.11a	
Monoterpene ethers			0.14 ± 0.01c	0.21 ± 0.00b	0.30 ± 0.02a	0.16 ± 0.01c	0.16 ± 0.01c	
Phenols			0.34 ± 0.01a	0.26 ± 0.00b	0.06 ± 0.02c	0.05 ± 0.00c	0.14 ± 0.00b	
Total			95.91 ± 1.22a	93.53 ± 1.08a	94.22 ± 1.13a	79.24 ± 0.88b	70.15 ± 1.54b	

Means in the same lines with a different letter (a–e) are significantly different at $P < 0.05$, (Duncan test). GC–MS, gas chromatography–mass spectrometry; – not detected, tr: trace.

[c] Order of elution in HP-5 MS column.

[a] Apolar HP-5 column.

[b] Polar HP Innowax column.

decreased under nozzle diameter 7 and 8 mm (0.05%) except for diameter 5 mm where their rates increased significantly and reached 0.34%.

To the best of our knowledge, the effect of nozzle diameter on essential oil composition is investigated for the first time in coriander cakes. For this reason, it is difficult to compare results of this study with other works. However, some works present the hydrodistillation extracting the highest number of compounds (Msaada et al., 2007; Telci et al., 2009) while others attribute a better performance to the conventional techniques (Mhemdi et al., 2011).

These authors showed that only sixteen compounds were identified in dried seeds before supercritical extraction. This could be explained by the evaporation of some of the volatile

compounds, such as camphene, α-thujene, 1,8-cineole, menthol, carvone, during drying.

Essential oil composition depends on many factors affecting the plant such as genetic structures and ecological conditions (Telci et al., 2006). For example, maturation stages constitute an important factor influencing essential oil composition in some plants (Telci et al., 2009).

In order to diagnose and characterise the correlation among the diameter nozzle of cake oil, the resulting dendrogram (Fig. 2), was useful for obtaining pre-selected profiles of high similarity. The data set was divided into two groups. The first cluster included trials of 8 and 9 mm of nozzle diameter. The second cluster can be subdivided into two subgroups: trials obtained with the nozzle of 5 and 7 mm in diameter; trials included the diameter 6 mm.

3.3. Antioxidant activity

In the present study, the antioxidant activities of coriander cakes obtained by the different trials as compared with BHT as reference antioxidant compound were determined, and the results are summarised in Table 2.

Free radical scavenging properties of methanolic extract from different trials are presented in Table 2. Lower IC_{50} value indicated higher antioxidant activity. All methanolic extracts of different coriander cakes (IC_{50} = 55 μg/ml for nozzle 5 mm, IC_{50} = 73 μg/ml for nozzle 7 mm, IC_{50} = 88 μg/ml for nozzle 9 mm) showed lower scavenging ability on DPPH radicals when compared to the synthetic antioxidant BHT (IC_{50} = 25 μg/ml).

The extract demonstrated a concentration dependent scavenging activity by quenching DPPH radicals; DPPH radical scavenging activities of coriander cake extract increased with increased the nozzle diameter. In this context, Shih et al. (2009) reported that the extrusion process significantly increased the DPPH radical scavenging activity in the different sweet potato extrudates. In the same way, Sharma et al. (2012) were also found the antioxidant activity increased significantly upon extrusion of barley. It has been proved that antioxidant activity of plant extracts is mainly ascribed to the concentration of the phenolic compounds present in the plants (Heim et al., 2002).

In this study, we evaluated the antioxidant activity of extracts of different trials of coriander cakes by the β-carotene-linoleate bleaching method because β-carotene shows strong biological activity and constitutes a physiologically important compound (Kumazawa et al., 2002; Sakanaka et al., 2005). This method is based on the loss of the yellow colour of β-carotene due to its reaction with radicals formed after linoleic acid oxidation in emulsion. The rate of β-carotene bleaching can be slowed down in the presence of antioxidants (Kulisic et al., 2004).

All extracts had lower antioxidant activities than BHA and BHT with IC_{50} ranging from 543 μg/ml of small nozzle (5 mm) and 610 μg/ml of bigger diameter (9 mm).

The reducing power of a bioactive compound may also serve as a significant indicator of its potential antioxidant activity (Roginsky and Lissi, 2005). Table 2 showed that the Fe^{3+} reducing power of cake trials differs greatly depending on nozzle diameter. The coriander cakes showed the lower reducing capacity (EC_{50} = 700 μg/ml) compared to that of the ascorbic acid (EC_{50} = 40 μg/ml).

3.4. Total phenolic, total flavonoid and total tannin contents of coriander cake

Phenolic compounds serve as important antioxidants because of their ability to donate a hydrogen atom or an electron in order to form stable radical intermediates. So, they prevent the oxidation of various biological molecules (Cuvelier et al., 1992). In addition, several oilseeds and their byproducts have been investigated for phenolic compounds in search for safe sources of natural antioxidants (Wettasinghe et al., 2002). In the case of cereal grains it has been shown that their outer layers such as husk and aleurone cells contain the highest concentration of total phenolics (Kähkönen et al., 1999).

Fig. 3 summarises the results from the quantitative determination of the tannins, flavonoids and total phenol contents of the different methanolic cake extracts. The total phenolic and flavonoid contents varied between different nozzle diameters; the highest values unregistered of small diameters (5 and 6 mm). The total phenol contents decreased significantly ($p < 0.05$) when increased the nozzle diameter and reached its lowest value (9.11 mg GAE/g) of 9 mm in diameter. In

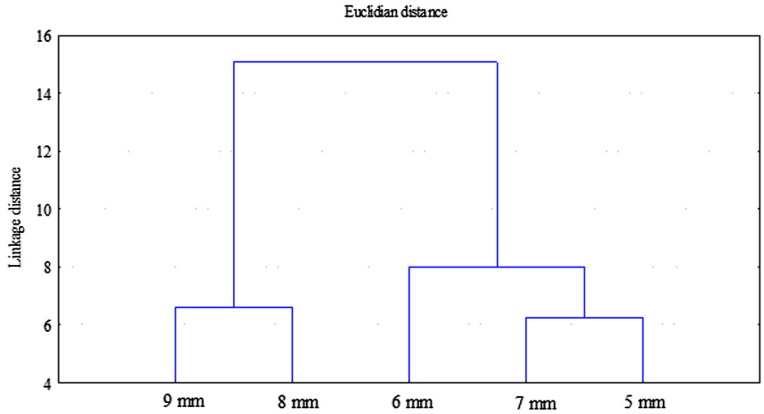

Figure 2 Two-dimensional dendrogram obtained from the cluster analysis of the essential oils of the different trial of *C. sativum* cake based on the data (Table 1): horizontal, samples analysed; vertical, differentiation level between samples. N: nozzle diameter (mm).

Table 2 Antioxidant activities of methanolic extract from coriander (*Coriandrum sativum*) cake.

	DPPH (IC_{50}, μg/ml)	β-Carotene bleaching (IC_{50}, μg/ml)	Reducing power (EC_{50}, μg/ml)
Nozzle diameter (mm)			
5	55 ± 0.33d	543 ± 1.02d	576 ± 1.33c
6	65 ± 0.21c	553 ± 0.99c	589 ± 1.21c
7	73 ± 0.87b	576 ± 1.67b	602 ± 1.87c
8	76 ± 1.14b	588 ± 1.34b	650 ± 1.65b
9	88 ± 1.54a	610 ± 1.54a	700 ± 2.43a
Synthetic antioxidant			
BHT	25 ± 0.20e	70 ± 0.57e	–
BHA	–	43 ± 0.15f	–
Ascorbic acid	–	–	40 ± 0.13d

IC_{50} value: the effective concentration at which the antioxidant activity was 50%. The absorbance was 0.5 for reducing power, the EC_{50} value was obtained by interpolation from linear regression analysis. Each value is expressed as mean SD ($n = 3$). Means with different capital letter within a row are significantly different ($P < 0.05$).

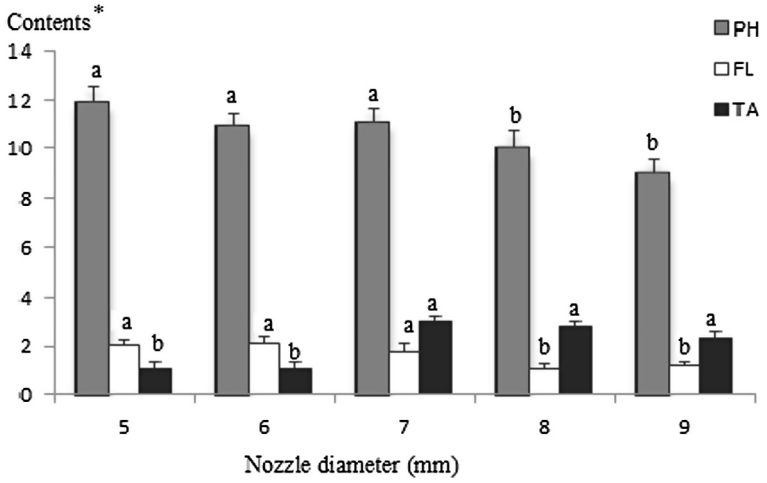

Figure 3 Total phenol (PH), flavonoid (FL) and tannin (TA) contents of different nozzle diameter from coriander cakes. * Total polyphenol and tannin contents were expressed by mg GAE/g DW and total flavonoid contents were expressed by mg CE/g DW. Values are represented as mean ± standard deviation of triplicates. The data marked with the different lower case letters in the histograms of each phenolic category share significant differences at $p < 0.05$ (ANOVA test).

the present study, total phenolic compound of coriander cake extract was found to be higher than sesame cake extract (1.94 mg GAE/g DW) (Mohdaly et al., 2011), potato peels (2.91 mg GAE/g DW) (Mohdaly et al., 2010), banana (2.32 mg GAE/g DW) (Nagendran et al., 2006), carrot (1.52 mg GAE/g DW) (Kequan and Liangli, 2006) and wheat bran (1.0 mg GAE/g DW) (Kähkönen et al., 1999). However, total phenol content in our study was found to be lower than black cumin seed cake (27.8 mg GAE/g). It has been reported that the reduction in total phenolic content may be attributed either to the decomposition of phenolic compounds due to the high extrusion temperature or alteration in molecular structure of phenolic compounds that may lead to reduction in the chemical reactivity of phenolic compounds or decrease their extractability due to certain degree of polymerisation (Altan et al., 2009).

A significant decrease in the total flavonoid content was observed under parameter of extrusion (Fig. 2). The highest values were observed with small nozzle diameter (5 and 6 mm) and reached 2 mg CE/g DW in coriander cake extracts. The lowest total flavonoid contents were signalled of nozzle diameter to 9 mm in cake extract with 1.18 mg CE/g DW. However, Mohdaly et al. (2011) found that the total flavonoid content in sesame cake extract was 0.88 ± 0.02 (mg QE/g DW). The decrease in total flavonoid content may be attributed to the thermal destruction of flavonoids, as this later are reported to be heat sensitive (Sharma and Gujral, 2011; Xu and Chang, 2008), therefore the total flavonoid content decreased upon extrusion cooking. In the same way, these results are in agreement with those previously reported by Im et al. (2003) and Huang et al. (2006) for buckwheat and sweet potato, respectively, upon thermal processing.

Significant differences were also found in total tannin contents among different nozzle diameters, the highest values were observed with nozzle diameter of 7 mm and reached 3.00 mg CE/g DW. Contrary to total phenol and flavonoid contents, total tannin contents increased under the increased nozzle diameter to 9 mm and reached 2.3 mg CE/g DW.

4. Conclusion

This study revealed coriander cake as a source of natural bioactive compounds and antioxidant activity which could be attractive to the food or pharmaceutical industry. The major essential oil compound in cake was linalool, which contributes greatly to the high antioxidant activities of this species. The qualitative variability observed in all trials suggests that essential oil composition in coriander cakes is greatly influenced by different nozzle sizes. Coriander cake contained high amounts of polyphenols, flavonoids and tannins contents and high antioxidant potential for producing specific health-promoting antioxidants in the food industry. Also, use of oil cakes offers good alternative to traditional applications by their exploitation in the production of environmentally friendly green biofuel. Another key point to be noted is that the bioprocess utilising oil cakes is attractive due to relatively cheaper availability of the oil cakes throughout the year, making it even more favourable when economics is considered.

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